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Electronic supplementary information

Visible light assisted photocatalytic mineralization of diuron pesticide using novel type II CuS/Bi₂W₂O₉ heterojunctions with hierarchical microspherical structure

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Materials

Copper nitrate trihydrate [Cu(NO₃)₂.3H₂O], bismuth nitrate pentahydrate [Bi(NO₃).5H₂O], ammonium tungstate [(NH₄)₁₀W₁₂O₄₁], urea [N₂H₄CO] and thiourea [N₂H₄CS] were purchase from Himedia India Ltd. Diuron pesticide was procured from Sigma Aldrich Ltd., India. All chemicals were of analytical reagent grade and used directly without any further purification.

Synthesis of Bi₂W₂O₉ nanomaterial (BWO)

The Bi₂W₂O₉ was synthesized by solution combustion method taking ammonium tungstate, bismuth nitrate as precursor salts and urea as fuel. The fuel to oxidizer ratio was maintained at 1. In a typical synthesis, required amount of Bi(NO₃)₃.5H₂O, (NH₄)₁₀W₁₂O₄₁ and urea were mixed well and made a paste by dropwise addition of distilled water. The mixture was transferred to a furnace pre-heated at 400 °C. The mixture instantaneously got ignited producing lot of gaseous product and a foamy solid. The combustion mixture was maintained at 400 °C for 30 minutes which was subsequently cooled, grinded to fine powder and calcined at 800 °C for 6 h to obtain the Bi₂W₂O₉ material.

Synthesis of CuS/Bi₂W₂O₉ heterojunction material (CuSBWO)

The CuS/Bi₂W₂O₉ heterojunction materials were synthesis by hydrothermal method by taking Cu(NO₃)₂.3H₂O as salt precursor and thiourea as sulphur source. In a typical synthesis, required amount of copper nitrate and 2.5 molar excess of thiourea were dissolved in 50 ml distilled water. To this solution 1 g of BWO material was added and stirred for 30 minutes

followed by 30 minutes of sonication. The aqueous suspension was then transfer to a 100 ml Teflon lined autoclave. The hydrothermal treatment was performed under autogeneous pressure at 150 °C for 24 h. After the hydrothermal treatment, the solid residue was collected by centrifugation and washed three times each with water and ethanol, respectively. The resulting material was dried in a hot air oven at 60 °C for 12 h to obtain the CuS/Bi₂W₂O₉ material. Using this procedure, CuS/Bi₂W₂O₉ materials with CuS contents of 5, 10, 15 and 20 wt % were prepared. The CuS/Bi₂W₂O₉ heterojunction materials are referred as CuSyBWO in the subsequent text, where 'y' represents the wt % of CuS present in the heterojunction material.



Fig. S1 (I) Variation of peak position with CuS content for (114) peak of pure (a) BWO, (b) CuS5BWO, (c) CuS10BWO, (d) CuS15BWO, (e) CuS20BWO and (II) Vegard plot indicating an increase in d_{114} spacing with CuS content.



Fig. S2 FTIR spectra of (a) BWO, (b) CuS5BWO, (c) CuS10BWO, (d) CuS15BWO and (e) CuS20BWO heterojunction materials.



Fig. S3 Plot of $[F(R)hv]^2$ as a function of photon energy (hv) in eV of (a) BWO, (b) CuS (c) CuS5BWO, (d) CuS10BWO, (e) CuS15BWO and (f) CuS20BWO heterojunction materials.



Fig. S4 FESEM images of hydrothermally treated $Bi_2W_2O_9$ material (a) in presence of and (b) in absence of thiourea at 150 °C for 24 h.



Fig. S5 Degradation efficiency of CuS20BWO catalyst for diuron degradation in presence of different oxidant (O_2 flow 30 ml/min, O_3 flow 30 ml/min, H_2O_2 200 µl).



Fig. S6 Photocatalytic efficiency of CuSBWO catalysts for diuron degradation (10 ppm DU, 200 μ l 30 % H₂O₂, 75 mg of catalyst) under natural sun light.



Fig. S7 GC/MS analysis of degradation products of diuron at different reaction time (a) pure diuron, (b) 10 min, (c) 1.5 h and (d) 3 h catalysed by CuS20BWO heterojunction.



Fig. S8 Photocatalytic degradation of diuron in presence of different radical scavenger catalysed by CuS20BWO heterojunction photocatalyst system.



Fig. S9 Reusability of CuS20BWO heterojunction photocatalyst for degradation of diuron.



Fig. S10 XRD profile of CuS20BWO heterojunction photocatalyst material (a) freshly prepared, and after (b) 1st, (c) 2nd, (d) 3rd and (e) 5th catalytic cycles.

Calculation of band position of CuSBWO heterojunction materials

The valence band (VB) and conduction band (CB) positions of CuSBWO heterojunction photocatalysts have been calculated by using the empirical equation 1;

$$E_{VB} = X + 0.5E_g - 4.5 \text{ and } E_{CB} = E_{VB} - E_g$$
 (1)

Where, E_{VB} and E_{CB} are the valence and conduction band edge potential (vs. NHE), X is the electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms, E_e is the energy of free electron on hydrogen scale (4.5 eV), and E_g is the band gap of the photocatalyst. The X value for CuS photocatalyst is 5.29 eV [1], whereas for $Bi_2W_2O_9$ photocatalyst, the value of X is 6.3 eV which is calculated using the equation 2;

$$X(M) = 1/2(A_f(M) + I_1(M))$$

Where, X(M) is arithmetic mean of the electron affinity (A_f) and the first ionization potential (I₁) of the atoms constituting the molecule. The detail calculation for the VB and CB are presented in the electronic supplementary file.

(2)

Calculation of "X" value for Bi₂W₂O₉ photocatalyst

The formula is used in reference to the standard hydrogen electrode potential.

$$X(M) = 1/2(A_f(M) + I_1(M))$$

Where, X(M) is arithmetic mean of the electron affinity and the first ionization potential of the atoms. A_f is the electron affinity and I₁ is the first ionization potential, respectively.

For instance, the electron affinity of 1 mole Bi is 91 kj. So it is converted to every atom and the unit is transformed to eV:

 $A_{f}(Bi) = 91 \times 1000/(1.6 \times 10^{-19} \times 6.02 \times 10^{23}) = 0.944 \text{ eV}$

 $I_1(Bi) = 7.289 \text{ eV}$

Thus, X(Bi) = 1/2(0.944 + 7.298) eV = 4.12 eV

Similarly, $A_f(W) = 0.82 \text{ eV}$, $I_1(W) = 7.98 \text{ eV}$,

X(W) = 1/2(0.82+7.98) eV = 4.4 eV

 $A_{f}(O) = 1.463 \text{ eV}, I_{1}(O) = 13.618 \text{ eV},$

X(O) = 1/2(1.41+13.618) eV = 7.5 eV

Thus, the electronegativity of the Bi₂W₂O₉:

 $X = [X(Bi)^{2*}X(Bi)^{2*}X(O)^{9}]^{1/13}$

 $[(4.12)^{2*}(4.4)^{2*}(7.5)^{9}]^{1/13} = 6.3 \text{ eV}$

Because the observed band gap of Bi₂W₂O₉ is found to be 3.0 eV,

 $E_{CB} = X - 0.5E_g - 4.5 = 6.3 - 3.0 \times 0.5 - 4.5 = 0.3 \text{ eV}$

 $E_{VB} = X + 0.5E_g - 4.5 = 6.3 + 3.0 \times 0.5 - 4.5 = 3.3 \text{ eV}$

References

[1] Y. P. Bhoi, S. R. Pradhan, C. Behera, B. G. Mishra, Visible light driven efficient photocatalytic degradation of congo red dye catalyzed by hierarchical CuS-Bi₂CuxW_{1-x}O_{6-2x} nanocomposite system. RSC Adv. 6 (2016) 35589-3560.